Molecular Dynamics Simulations of Aqueous Species in the System H_2O-CO_2-NaCl over Wide Ranges of Temperatures, Pressures, and Compositions

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We have undertaken molecular dynamics (MD) computer simulations of CO_2-H_2O-NaCl fluids and carbonate and bicarbonate aqueous solutions over a range of temperatures, pressures and compositions relevant to many geochemical and technological applications such as geological sequestration of CO_2 in saline aquifers and water desalination. Molecular modeling is an especially promising approach for molecular-level understanding of the properties of such carbon-bearing aqueous fluids because their structures are not readily studied experimentally using conventional X-ray or EXAFS methods. In this case, experimental methods produce ambiguous results, because the C and O atoms of the solute species are not distinguishable from O atoms of solvent H_2O. MD simulations of 0.5m Na_2CO_3 and 0.5m and 1.5m $NaHCO_3$ aqueous solutions under near-ambient conditions show that their structures, hydration energies, and thermodynamic behavior are quite different. In Na_2CO_3 solutions, relatively stable ionic clusters of Na^+ and CO_3^{2-} are formed, and long simulation runs were necessary to effectively probe the structure, energetics, and dynamics of these clusters. Due to the ion cluster formation, the diffusion rates of both Na^+ and CO_3^{2-} are ~3-6 times lower than in similar sodium chloride solutions. In contrast, in $NaHCO_3$ solutions, ions cluster much less, and the diffusion rate of HCO_3^- is thus about the same as that of Cl^-. The hydration shells of carbonate and bicarbonate ions both contain approximately 10 water molecules, but the carbonate one is more structured due to the higher anion charge. H_2O-rich and CO_2-rich compositions of the ternary CO_2-H_2O-NaCl system also demonstrate strikingly different behavior. In dense CO_2-rich fluids, dissolved H_2O molecules exhibit a high degree of hydrogen bonding and form relatively stable H-bonded clusters. In contrast, CO_2 molecules dissolved in water-rich fluids occur in clathrate-like cages formed by surrounding H-bonded water molecules.